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(72) Inventor REINHARD ERNST VOGEL

(54) IMPROVEMENTS RELATING TO RADIATION SHIELDS

(71) We, FRIEDRICH MARXEN and REINHARD ERNST VOGEL, both citizens of Germany, of Vaduz, Liechtenstein, Banholzstrasse 418, Germany and Munchen-Harlaching, Terhallestrasse 37, Germany, respectively, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to material effective as shielding against radioactive rays, and to methods for producing such material.

In our Patent 1,110,181 there is claimed and described a body formed of cement or concrete (including magnesia cement or concrete), internal or external plaster, asbestos cement or gypsum, which bodies are effective as shielding against radioactive rays, especially gamma and neutron radiation, characterised by a 2.5—35% content of one or more lead, bismuth, tungsten, zirconium, iron, tin, cadmium, lithium or barium compounds of stearic acid and/or medium and/or higher saturated fatty acids. "Medium" and "higher" saturated fatty acids are defined as having 9 or more carbon atoms to the molecule.

Preferably the saturated fatty acid has at least 16 carbon atoms: good results are obtained with palmitic, stearic, arachidic, behenic or montanic acids. Lead compounds of stearic or montanic acids are particularly advantageous. The fatty acids may be produced synthetically or may be mixtures.

This invention concerns an improvement in or modification of the invention of our abovementioned Patent. In broad terms, our invention concerns the application of the abovementioned metal compounds of saturated fatty acids to the production of bodies, effective as radioactive shields, comprising natural or synthetic rubber and/or synthetic resin.

The invention provides a body, for example, a plate, coating, or flexible sheeting having a shielding effect against radioactive radiation, particularly gamma and neutron radiation, said body consisting essentially of a material selected from the group consisting of natural and synthetic rubbers and the synthetic plastics material referred to below, the body having distributed therethrough and intimately mixed therewith an effective amount, being between 10 and 60% of the weight of the body, of at least one compound of a saturated fatty acid which acid is solid at room temperature and has at least 9 carbon atoms with at least one metal selected from the group consisting of lead, bismuth, tungsten, zirconium, iron, tin, cadmium, lithium and barium. The invention also includes a method of producing the body just defined comprising the steps of forming an intimate mixture of said at least one compound of saturated fatty acid and of said material in polymerizable form; and subjecting said polymerizable material with said fatty acid compound admixed thereto to polymerization.

The synthetic plastics materials referred to are polyurethanes, polyamides, polyethylene, polyfluoroethylene, polypropylene, epoxy resins, unsaturated polymerizable polyesters, polyvinyl chloride, polyvinyl fluoride, copolymers of polyvinyl fluoride and polyvinyl chloride, polystyrene and copolymers thereof, and methacrylate resins.

Of the synthetic rubbers, it is particularly preferred to utilize polyisobutylene, butadiene-styrene polymerizates, chloroprene and alkylpolysulfides.

Preferably the effective amount of the compound of the saturated fatty acid will be equal to between about 10 and 40% of the weight of the body.

According to certain preferred embodiments of the present invention, the body additionally includes effective amounts of at least one finely subdivided substance selected from the group consisting of lead and lead compounds, tungsten and tungsten oxides, iron and iron compounds, boron and boron compounds, cadmium, cadmium oxide and cadmium sulfide. Some suitable compounds are mentioned in our abovementioned Patent 1,110,181.

Preferably, the additional finely subdivided substance is of colloidal particle size. Suitable

boron compounds include boron carbide, boric acid and boron trioxode.

Preferably, the body of the present invention is formed by first producing an intimate mixture of the fatty acid compound and of the synthetic material or natural rubber in polymerizable and thus hardenable form, followed by subjecting the thus-formed mixture to polymerization of the polymerizable component thereof.

As briefly described above, fatty acid compounds with certain metals, specifically compounds of fatty acids which acids are solid at room temperature and have at least 9 carbon atoms, with at least one metal selected from the group consisting of lead, bismuth, tungsten, zirconium, iron, tin, cadmium, lithium and barium may be incorporated into a great number of synthetic rubbers in order to endow bodies formed thereof with an effective shielding effect against radioactive radiation as well as against alpha, beta, gamma, ionic and neutron radiation.

Of these types of radiation, gamma rays and neutrons are the most dangerous ones. Gamma rays are primarily absorbed by elements of high density and a high number in the periodic system, whereas neutrons which do not carry a charge interact with lighter elements, particularly hydrogen, and also carbon and oxygen, i.e., with elements of which synthetic plastic materials are generally composed or which at least form a very substantial part of the synthetic plastic materials.

Upon such contact, elastic and non-elastic collisions occur which reduce the kinetic energy of the neutrons, and collisions which cause absorption and possibly the formation of beta, gamma, and ionic radiation.

By incorporating the abovementioned fatty acid compounds into the polymeric material, the number of hydrogen atoms available for slowing down and absorption of neutrons is greatly increased whereas the heavy metals will absorb the impinging or formed gamma rays. This is particularly important in the case of synthetic materials since radiation thereof tends to reduce and impair their mechanical properties or even to destroy the same. The radiation protection by means of synthetic materials, in the form of plates, blocks, sheets, lacquer coatings and the like, is important particularly since some of these polymeric materials can be intimately and firmly bound to concrete, steel, iron, aluminium and the like, whereas the resilient polymeric materials, particularly the natural and synthetic rubbers, due to their flexibility and/or resiliency, are highly useful for producing protective clothing, such as aprons, thereof.

It has been found, however, that the desired results are achieved to a satisfactory extent only with a certain group of plastic materials, partially because the fatty acid compounds cannot be incorporated or can only be difficultly incorporated into certain plastic materials and partially because some of the plastic materials will be so much reduced in their mechanical properties, such as tear and bending resistance when exposed to alpha, beta, gamma, ionic or neutron radiations that the materials become brittle or are destroyed.

For these reasons, the present invention is generally not concerned with improving the shielding effect of cellulose esters and ethers, polycarbonates, silicone resins, polymethylene oxide resins, phenolic resins, "galalith" (Registered Trade Mark) and vulcanised fibers.

On the other hand, the present invention is excellently suitable for producing a shielding effect by incorporating the fatty acid compounds described above into polyurethanes, polyamides, polyethylene, polyfluoroethylene, polypropylene, epoxy resins, unsaturated polymerizable polyesters, and natural and synthetic rubbers.

Furthermore, good results, although sometimes not quite as good as those which are achieved with the group of polymeric materials mentioned above, may also be obtained with polyvinyl chloride, polyvinyl fluoride, copolymers of polyvinyl chloride and polyvinyl fluoride, polystyrene and copolymers thereof and methacrylate resins.

Of the synthetic rubbers, it is particularly preferred to utilize polyisobutylene, and good results were also obtained with butadiene-styrene and polymerizates, chloroprene and alkyl-polysulfides.

The proportion of metal-fatty acid compounds relative to the synthetic polymeric materials or rubbers (natural or synthetic) depends on the specific polymeric materials and the specific fatty acid compounds which are utilized; preferably the proportion is between 10 and 40% of the weight of the finished product.

Upon working up of the mixtures on extrusion devices or calenders, the metal-fatty acid compounds will simultaneously serve as stabilizing lubricants and, in the case of rubbers, for increasing the resiliency thereof so that for instance the incorporation of relatively very large proportions of lead powder is possible while still maintaining the desired resilient characteristics of the material. These advantages are obtainable particularly with respect to the two last mentioned groups of preferred and utilizable polymeric materials whether they are natural rubbers or synthetic polymers.

By further additions of pulverulent lead and its compounds, for instance lead oxides or lead sulfide but also others, tungsten and its oxides, iron and its oxides, preferably in finely pulverulent or collidal form, the shielding effect against gamma rays will be increased, whereas the additional incorporation of boron compounds, preferably boron trioxide, boron carbide, an alloy of boron carbide and alum-

inium, and boron nitride, as well as cadmium and cadmium compounds, for instance cadmium oxide and cadmium sulfide, will increase the absorption of the decelerated neutrons. Boron may also be utilized in the form of esters of boric acid with higher alcohols such as glycerol boric acid ester, combined with or together with stearic acid. The proportion of such additional pulverulent or colloidal additives relative to the proportion of the metal-fatty acid compounds will again depend on the specific type of the natural rubber or synthetic polymeric material as well as the degree of shielding effect required and the desired mechanical strength and characteristics of the rubber or synthetic polymeric material. Generally, the proportions of these pulverulent additives of preferably colloidal dimensions, may be the same or even greater than the percentage of the metal fatty acid compounds.

The shaped bodies having a shielding effect, which are obtainable according to the present invention, may be prepared by introducing the metal-fatty acid compounds and possibly the further additives described above into the polymerizable synthetic materials, or the natural rubber, while the latter are in liquid form, and thereafter causing polymerization of the polymerizable fraction of the thus-formed mixture. In the case of natural and synthetic rubbers, the addition of the metal-fatty acid compounds and, if desired, the further additive is preferably carried out during vulcanization or mastication.

The following examples are given as illustrative only without, however, limiting the invention to the specific details of the examples.

Example 1

100 parts by weight epoxy resin are mixed in a heated stirring device with 50 parts by weight lead stearate and 50 parts by weight lead of finely pulverulent to colloidal size. Mixing is carried out at 125°C., and thereafter 80 parts by weight of hexahydrophthalic acid are added.

After thorough mixing, the thus-formed mixture is cast into plates having a thickness of 20 mm.

Example 2

100 parts by weight epoxy resin are mixed in a heatable stirring device with 20 parts by weight of lead stearate, 10 parts by weight of finely subdivided or colloidal lead powder and 10 parts by weight boron trioxide. The mixing is carried out at 110°C. Thereafter, 11 parts by weight diethylene triamine are incorporated into the mixture and the latter then poured onto steel plates.

Example 3

100 parts of granulated polyethylene having an edge length of 3—4 mm. and a density of 0.93 are intimately mixed with 20 parts by weight cadmium stearate and 7 parts by weight boron carbide and the thus formed mixture is then melted under pressure in a heated mould at 130—135°C. and compressed into plates having a thickness of 60 mm. After cooling, the plates are removed from the mould.

Example 4

A solution is made comprising 100 parts of unsaturated polyester resin which is formed of saturated and unsaturated dicarboxylic acids with divalent alcohols in molar relationship and, calculated on the amount of said unsaturated polyester resin, 25% styrene and 5% allyl ethers of polyvalent alcohols: this solution is mixed with 30 parts by weight lead stearate and 10 parts by weight butyl acetate. Thereafter 0.5 parts by weight benzoyl peroxide and 0.05 parts by weight of cobalt naphthenate are admixed.

After thorough mixing, the entire mixture is applied to a support in the form of a lacquer layer having a thickness of four millimeters.

Example 5

100 parts by weight chloroprene, for instance the type commercially available as "Neoprene AC" are calendered on a heatable calender. Over a period of ten minutes there are added in the indicated sequence:

2.5 parts by weight active zinc oxide, 30.0 parts by weight lead montanate, 20.0 parts by weight colloidal lead powder, and 3.0 parts by weight of boron trioxide.

Calendering is carried out until a uniform mixture is obtained, and to the desired thickness.

WHAT WE CLAIM IS:—

1. A body having a shielding effect against radioactive radiation, particularly gamma and neutron radiation, said body consisting essentially of a material selected from the group consisting of natural and synthetic rubbers and the following synthetic plastics materials: polyurethanes, polyamides, polyethylene, polyfluoroethylene, polypropylene, epoxy resins, unsaturated polymerizable polyesters, polyvinyl chloride, polyvinyl fluoride, copolymers of polyvinyl chloride and polyvinyl fluoride, polystyrene and copolymers thereof, and methacrylate resins, the body having distributed therethrough and intimately mixed therewith an effective amount, being between 10 and 60% of the weight of the body, of at least one compound of a saturated fatty acid which acid is solid at room temperature and has at least nine carbon atoms with at least one metal selected from the group consisting of lead, bismuth, tungsten, zirconium, iron, tin, cadmium, lithium and barium.

2. A body as defined in Claim 1, wherein said material includes a synthetic rubber selected from the group consisting of chloro-